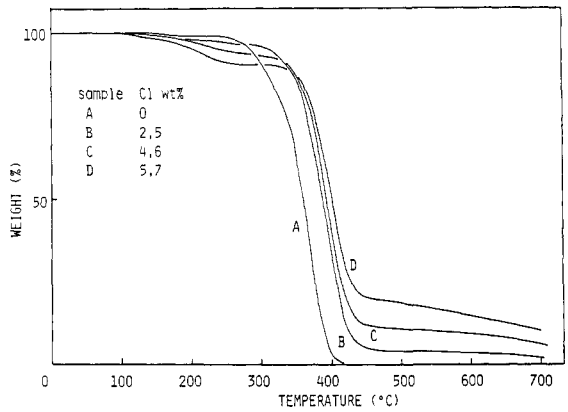

Figure 6. TGA weight loss curves of chloromethylated ST–DVB copolymers.

from the other two types of chloromethyl-substituted polystyrenes.

Relationships between chlorine content and peak intensities of the characteristic pyrolyzates for the chloromethylated ST–DVB copolymers derived from Table II are shown in Figures 5a–c. As shown in Figure 5a, peak intensities of ST monomer decrease almost linearly with the rise in the chlorine content for the chloromethylated ST–DVB copolymers. Generally, similar relationships are observed between chlorine content and peak intensities of the characteristic products for the other copolymers. Consequently, these relationships could be used as calibration curves for determining the degree of chloromethyl substitution for corresponding copolymer systems.

The Cl-MST peaks observed for both ST–Cl-MST–DVB and chlorinated *p*-MST–DVB copolymers are not observed for chloromethylated ST–DVB copolymers. This phenomenon might be closely related to the methylene cross-linking formed during the Friedel–Crafts chloromethylation.[4] In connection with this phenomenon, the total peak intensities of ST monomer, dimer, and trimer for the chloromethylated ST–DVB copolymers are smaller than those of the ST–Cl-MST–DVB copolymers of corresponding chlorine content for the samples with larger chlorine content (Table II).

Typical TGA weight loss curves of the chloromethylated ST–DVB copolymers are shown in Figure 6. Generally, the weight loss occurs stepwise. The first weight loss, occurring around 200 °C, increases as the degree of chloromethylation increases. The main degradation, occurring around 400 °C, shifts to higher temperature, and the amounts of residue increase as the decrease of chloromethylation increases, even though the degree of DVB cross-linking, which primarily affects the thermal stability of the network, is essentially the same. These phenomena suggest that dehydrochlorination occurs around 200 °C, and the residue with a methylene cross-linked structure undergoes further degradation around 400 °C. In connection with this, chlorine-containing pyrolyzates observed by PyGC for either copolymer system are relatively small, considering the chlorine contents of the original copolymers and the recovery rates in PyGC shown in Table II decreased as the chlorine content increased.

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Registry No. (ST)(*p*-Cl-MST)(*m*-Cl-MST)(DVB) (copolymer), 80531-81-3.

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Direct NMR Observation of Model and Macromolecular Esters in Polymerization of Styrene by Perchloric Acid

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ABSTRACT: 1-Phenylethyl perchlorate (1) was prepared from 1-phenylethyl bromide and $AgClO_4$ directly CD_2Cl_2–C_6D_6 (2:1) solvent mixture and observed directly by ^1H NMR at −78 °C. 1 decomposes at temperatures above −40 °C via Friedel–Crafts alkylation. It reacts with water at −78 °C to form bis(1-phenylethyl) ethers. In the reaction with styrene 1 is converted to macromolecular ester. The ^1H NMR absorption of the macromolecular perchlorate is shifted upfield in comparison with 1 because of the diamagnetic shielding by adjacent aromatic rings.

Introduction

The term "pseudocationic" polymerization was introduced more than 20 years ago to describe propagation via covalent esters in the polymerization of styrene initiated by perchloric acid,[1] but up to now neither macromolecular ester nor its low molecular weight analogue, 1-phenylethyl perchlorate, has been observed directly.

Recently several new well-defined polymers were prepared from monomers which are known to polymerize exclusively through ionic mechanisms by using initiators with counterions forming covalent bonds with active centers.[2] These polymers (polyacrylates or poly(vinyl ethers))

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have controlled molecular weights, low polydispersities, and required functionalities indicating living polymerization (transferless and terminationless process). The pseudocationic polymerization of styrene,[1] which resembles the above systems, may lead to similar well-defined polymers providing that no ionic intermediates are involved in propagation and that monomer is consumed by covalent active centers.[3] Therefore it is important to determine the structure and proportion of the active centers in this as well as in the other systems.

Originally pseudocationic polymerization was proposed for a styrene–perchloric acid system in order to explain the absence of the UV absorption of carbenium ions, low sensitivity to water, and simple kinetic behavior.[1] The subsequent detailed studies revealed the bimodality of the molecular weight distribution and showed that the high molecular weight fraction was formed by conducting chain carriers (free ions).[4,5] The short-lived carbenium ions were later detected by using a stopped flow technique.[6] The first evidence supporting the presence of covalent active centers was the absence of free acid during the polymerization.[7,8] The efficient formation of block copolymers with *N*-tert-butylaziridine at low temperatures[9] and the end-capping with naphtoxide anions also indicated the presence of esters as the end groups.[10] Nevertheless the attempts to directly observe perchlorate esters in polymerization as well as in model systems were unsuccessful.[1,11] These failures were ascribed to the nonoptimized reaction conditions and to poor ^{1}H NMR resolution[12] but might have been also due to the low stability of the ester, e.g., to its autocatalytic decomposition by the excess acid.[13] The aim of this study was to synthesize and spectroscopically characterize the model and macromolecular perchlorate esters and to study some of their basic chemical reactions.

Results

Synthesis and Stability of 1-Phenylethyl Perchlorate. 1-Phenylethyl esters could be prepared in the reaction of (1-phenylethyl)carbinol with protonic acids, anhydrides, and acyl chlorides, in the reaction of the acid and styrene, and in the reaction of 1-phenylethyl halides and the corresponding silver salts. The latter method was successfully used for reactive esters such as tosylates, which form low nucleophilic anions.[14] We have chosen the same route for perchlorates to avoid side reactions such as polymerization (styrene and perchloric acid) or ether formation (anhydride and carbinol).[15,16]

1-Phenylethyl perchlorate was claimed to be formed in the reaction between 1-phenylethyl bromide and silver perchlorate in dichloromethane but was neither directly observed nor isolated.[1] The ester decomposed rapidly in the absence of excess monomer.[1,2] We have used a similar system, but the reaction was carried out at low temperatures (below −70 °C).

Silver perchlorate has a very low solubility in dichloromethane. The heterogeneous reaction with alkyl halides led to low ester yields and the formation of the insoluble silver halide on the surface of the silver perchlorate. Silver salts are soluble in aromatic solvents, because Ag^+ forms π-complexes with aromatics. Therefore we have used benzene–dichloromethane (1:2) mixtures. Solutions of $AgClO_4$ were soluble down to −78 °C at concentrations lower than $[AgClO_4]_0 < 0.07$ mol/L. 1-Phenylethyl bromide was distilled on vacuum line directly to the NMR tubes containing solutions of $AgClO_4$ in the mixtures of deuteriated benzene and dichloromethane frozen in liquid nitrogen. The reaction was then followed directly by NMR at −78 °C. Immediately after the contents of the tube were melted at −78 °C, silver bromide was precipitated. In the NMR spectra, in addition to the excess 1-phenylethyl bromide (5.05 ppm (q) and 1.95 ppm (d)), dichloromethane (5.00 ppm), and benzene (7.35 ppm), new signals were observed at 5.83 ppm (q) and 1.61 ppm (d) (cf. Figure 1). The proportion of these signals and their chemical shifts indicates the quantitative formation of 1-phenylethyl perchlorate:

$$PhCH(CH_3)Br + AgClO_4 \rightarrow AgBr\downarrow + PhCH(CH_3)OClO_3 \quad (1)$$

The chemical shifts of the methine protons in different 1-phenylethyl derivatives depend strongly on the structure of the parent anion (cf. Table I). Esters absorb at lower fields than halides and ethers. Generally the downfield

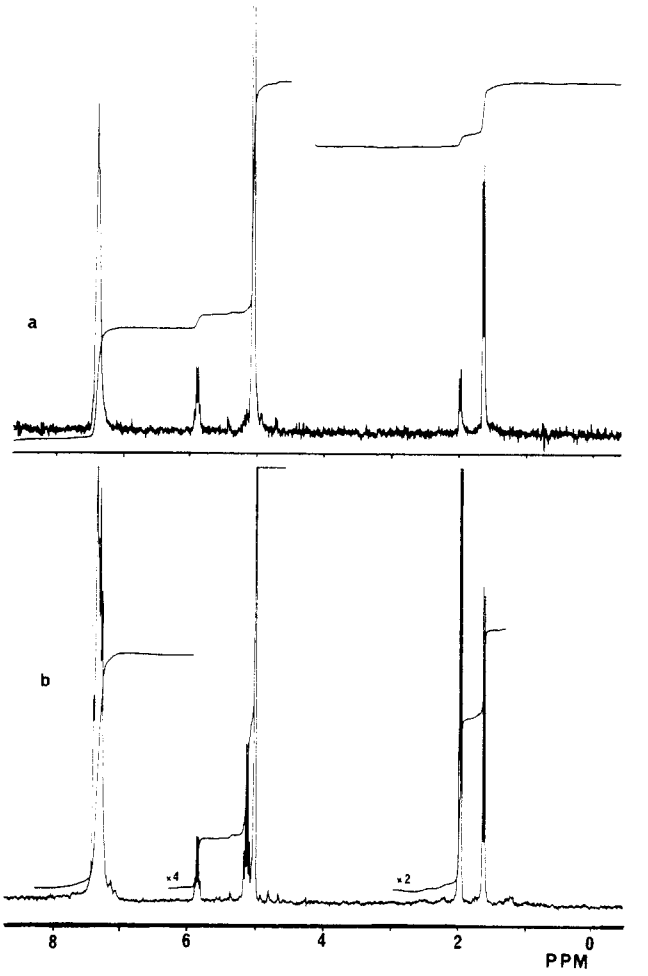


Figure 1. ^{1}H NMR (300 MHz) spectra of the mixture $[AgClO_4]_0$ = 0.036 mol/L and $[PhCH(CH_3)Br]_0$ = 0.042 mol/L (a) and $[AgClO_4]_0$ = 0.036 mol/L and $[PhCH(CH_3)Br]_0$ = 0.110 mol/L (b) in CD_2Cl_2–C_6D_6 (2:1) solvent mixture at −78 °C after 10 min.

Table I
^{1}H NMR Chemical Shifts[a] of Different 1-Phenylethyl Derivatives $PhCH(CH_3)X$ in CD_2Cl_2–C_6D_6 (2:1) Solvent Mixtures

X	δ, ppm	X	δ, ppm
ClO_4	5.83	Br	5.05
CF_3CO_2	5.85	Cl	4.75
CCl_3CO_2	5.81	OR[b]	4.5
CH_3CO_2	5.70	Ph	4.1

[a] As reference the chemical shift of the incompletely deuteriated dichloromethane was used (5.0 ppm, determined independently in a CD_2Cl_2–C_6D_6 mixture (2:1)). [b] When R = 1-phenylethyl two diastereoisomeric ethers (meso and racemic) absorb separately at 4.50 and 4.21 ppm, respectively.

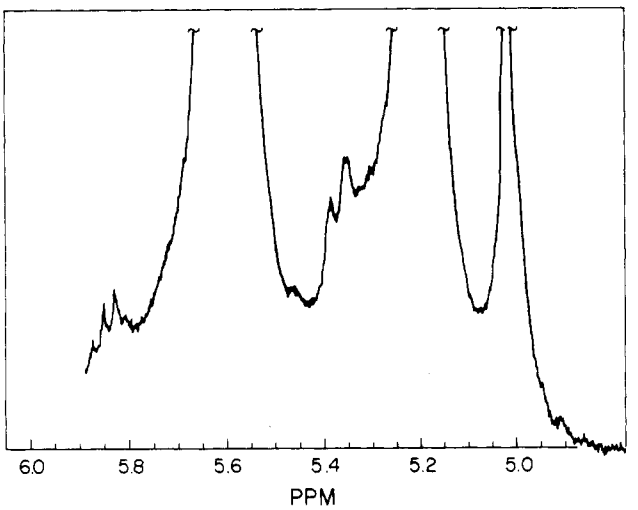


Figure 2. ^{1}H NMR (300 MHz) spectrum of the mixture $[AgClO_4]_0$ = 0.036 mol/L, $[PhCH(CH_3)Br]_0$ = 0.040 mol/L, and $[C_6H_5C{-}H{=}CH_2]_0$ = 1.0 mol/L in CD_2Cl_2–C_6D_6 (2:1) solvent mixture at −78 °C after 3 min.

shift is observed for the methine protons bound to better leaving groups. α- and β-hydrogen atoms for halides do now follow this rule. For example, the following chemical shifts (ppm) for methylene and methyl hydrogens in ethyl esters and halides were measured:[17] CF_3SO_3 4.33, 1.50; CF_3CO_2 4.35, 1.49; CH_3CO_2 4.10, 1.24; I 3.18, 1.86; Br 3.44, 1.70; Cl 3.60, 1.50. We have observed a similar pattern for perchlorate and bromide.

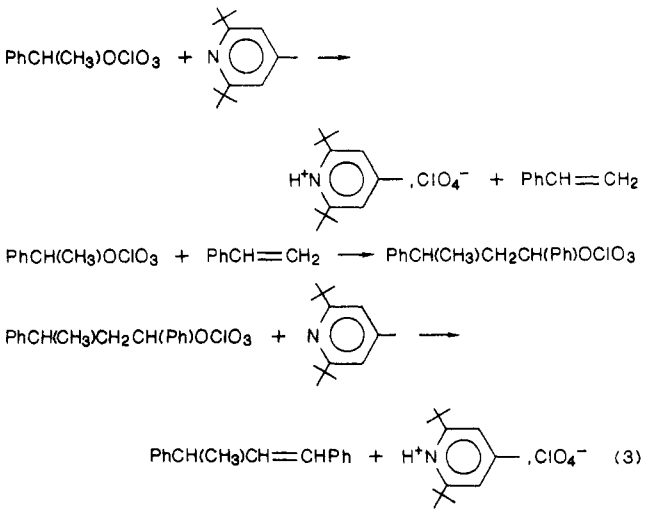
1-Phenylethyl perchlorate is stable at −78 °C for a long time (more than 2 h). At higher temperatures it decomposes and at −40 °C it disappears after less than 1 h. The main decomposition pathway is a Friedel–Crafts alkylation. In addition to oligomeric products formed by alkylation at the para position, cyclic dimer (9,10-dihydro-9,10-dimethylanthracene) was formed by the alkylation at the ortho position followed by cycloalkylation at the other ortho position. The low strain of the six-membered dimer accelerates this reaction.

Reaction with Water. Previous reports showed low sensitivity of the kinetics of polymerization of styrene by perchloric acid to water, which was used in concentrations comparable to the acid. These results are surprising in light of the high reactivity of the discussed esters. Therefore we studied the reactions of 1-phenylethyl perchlorate with a controlled amount of water. Reaction of perchlorate esters with the equimolar amount of water was completed in less than 3 min even at −78 °C and led to a mixture of racemic and meso bis(1-phenylethyl) ethers:

$$2PhCH(CH_3)OClO_3 + H_2O \xrightarrow[-2HClO_4]{} PhCH(CH_3)OCH(CH_3)Ph\ (RS)\ (+\ PhCH(CH_3)OCH(Ph)CH_3\ (RR\text{ and }SS)) \quad (2)$$

These ethers were previously observed and identified in the reaction of 1-phenylethanol with triflic anhydride.[18] The exact mechanism of reaction 2 is not known, but it should proceed by the formation of the intermediate carbinol and the subsequent reaction with ester (cf. eq 5). A similar mechanism was proposed for the reaction with optically active carbinol.[18] Methine protons in the racemic ether are more strongly shielded by the neighboring aromatic rings and absorb in a higher field. This phenomenon has the origin in the preferential trans,trans conformation, which also dominates for 2,4-diphenylpentanes,[19] a species with a structure analogous to those of the discussed ethers. In the trans,trans conformation both methine protons are efficiently shielded by phenyl rings. In the meso isomer only one methine proton can be shielded, leading to the overall lower shielding and higher value of the chemical shift.

Reaction with Hindered Pyridine. 2,6-Di-*tert*-butyl-4-methylpyridine is known as a very effective proton trap.[20,21] On the other hand, because of the steric hindrances of two ortho *tert*-butyl groups, it is usually inert toward more bulky electrophiles. We decided to study the stability of 1-phenylethyl perchlorate in the presence of pyridine in order to trap the traces of the acids that could catalyze decomposition of the ester. Esters form complexes with Lewis and protonic acids. Protonation activates the esters and may accelerate the Friedel–Crafts alkylation. Indeed, in the presence of the hindered pyridine no alkylation products were observed in the NMR spectra. However, the ester decomposed after 2 h at −30 °C to the unsaturated dimer 1,3-diphenyl-1-butene:



Reaction between 1-phenylethyl perchlorate and styrene was shown as a one-step process although it can involve ionization of the ester and ususal addition of styrene to carbenium ion followed by the rapid collapse of counterions to the dimeric ester. The formation of the linear dimer may indicate the abstraction of the β-protons by pyridine and the subsequent reaction of the produced styrene with the active center, followed by the next abstraction of the β-proton from the dimeric species. Another possibility is that the ester is in equilibrium with a small amount of olefin and the acid, which is effectively trapped by the hindered pyridine.

Reaction with Styrene. Formation of Macromolecular Ester. We have attempted the reaction of 1-phenylethyl perchlorate with styrene in the presence of a small amount of hindered pyridine. The pyridine quantitatively traps traces of the acid, which could lead to the rapid consumption of monomer by the usual (ionic) mechanism. At −70 °C, the reaction proceeds slowly and the apparent rate constant of propagation is $k_p \approx 10^{-2}$ mol^{-1} L s^{-1} (assuming first-order kinetics in monomer and initiator). This rate constant, as indicated by one of the reviewers, "fits very well with the value one could extrapolate from the kinetic data of ref. 1", suggesting that this "corroborates propagation by ester". However, this also fits the propagation on the ions in equilibrium with inactive covalent species, the apparent activation energy being the sum of the enthalpy of equilibrium and true activation energy of ionic propagation. Therefore it is impossible to establish the mechanism of propagation

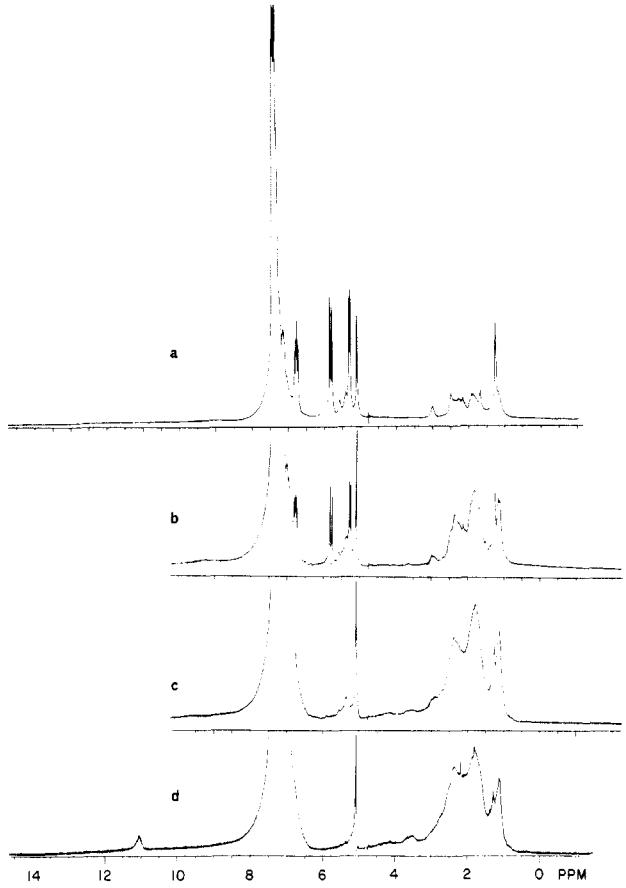


Figure 3. ^{1}H NMR (300 MHz) spectra of the mixture $[AgClO_4]_0$ = 0.036 mol/L, $[PhCH(CH_3)Br]_0$ = 0.035 mol/L, and $[C_6H_5C{-}H{=}CH_2]_0$ = 0.2 mol/L in CD_2Cl_2–C_6D_6 (2:1) solvent mixture at −70 °C after 15 min (a), 60 min (b), 3 h (c), and 8 h (d).

exclusively on the basis of these kinetic measurements.

In Figure 2 the region of active species is shown. In addition to two huge signals of the olefinic protons in the unreacted styrene, a quartet at 5.85 ppm and a triplet at 5.35 ppm can be observed on the shoulders of the monomer signals. The former absorption is ascribed to the methine proton in the 1-phenylethyl perchlorate and the latter to macromolecular perchlorates. The downfield shift observed for the dimeric and the growing species has its origin in the shielding by the adjacent aromatic nuclei (cf. Discussion). Chemical shifts of dimeric esters differ slightly from those of trimeric and larger macroesters (similar spectra were observed for oligomeric trifluoroacetates[22]). When relative concentration of ester was higher ($[M]_0/[ClO_4^-]_0$ = 7) it was possible to observe two sets of methine protons (Figure 3). Increase of the relative intensity of the upfield signal might indicate that it corresponds to the higher oligomers whereas the signal at 5.5 ppm comes from the dimeric species. Difference in chemical shifts might have also the origin in the meso and racemic structure of the macroester. These signals remain even after complete monomer consumption but disappear after 8 h at −70 °C.

We have also studied the reaction between 1-phenylethyl perchlorate and deuteriated styrene-d_8 (>98%). In such a system no signals of the growing species could be observed, but nondeuteriated end groups formed in initiation were found. In addition to the doublets of the methyl groups (meso and racemic), singlets of hindered pyridine (1.5 and 2.4 ppm), and a typical pattern of excess 1-phenylethyl bromide, the broad signals of the nondeuteriated polystyrene were found at 1.1 ppm. This indicates deprotonation of the ester and formation of the nondeuteriated styrene, which later is incorporated into the polymer chain simultaneously with deuteriated monomer:

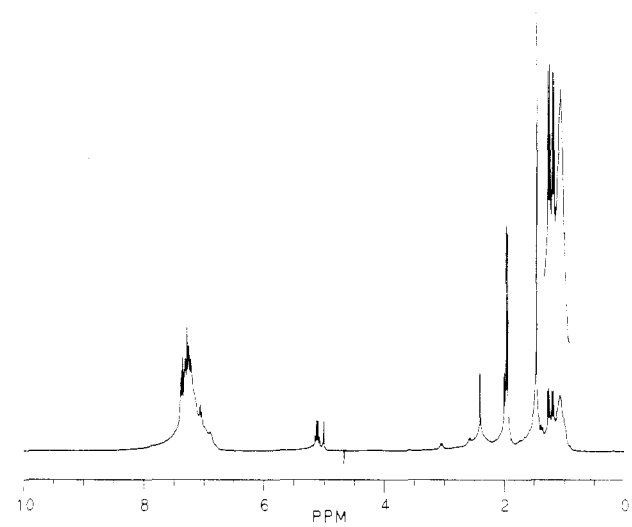
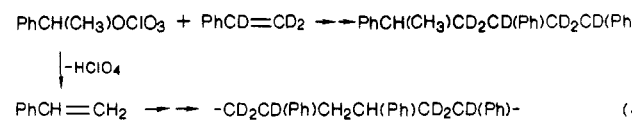


Figure 4. ^{1}H NMR (300 MHz) spectrum of the mixture $[AgClO_4]_0$ = 0.036 mol/L, $[PhCH(CH_3)Br]_0$ = 0.095 mol/L, [2,6-di-*tert*-butyl-4-methylpyridine]$_0$ = 0.010 mol/L, and $[C_6D_5CD{=}CD_2]_0$ = 1.0 mol/L in CD_2Cl_2–C_6D_6 (2:1) solvent mixture at −50 °C after 60 min.



This reaction carried out in the presence of hindered pyridine does not mean that ester must react directly with styrene. It can as well ionize prior to the monomer addition. A similar reaction with 1-phenylethyl trifluoromethanesulfonate formed in situ gave a much lower proportion of doublets of the methyl groups, which indicated lower stability of the latter ester.

Discussion

These studies give the first direct spectroscopic evidence for the existence of 1-phenylethyl perchlorate and the corresponding macromolecular ester. Although there are a few indirect indications supporting the formation of covalent species in the polymerization of styrene initiated by perchloric acid, our results show for the first time the presence of the macromolecular ester as well as the low molecular weight model in a CD_2Cl_2–C_6D_6 mixture (2:1). It is possible that the ester is more stable in a less polar solvent mixture than in pure CH_2Cl_2.[1] Our earlier attempts to prepare 1-phenylethyl trifluoromethanesulfonate under identical conditions were unsuccessful. The latter ester decomposed rapidly even at −78 °C. Studies with the optically active carbinol revealed that racemization of the ester (ionization) occurred before reaction with the strongly nucleophilic carbinol. The present results confirm our earlier observations. The proportion of the end groups $CH_3CH(Ph)$--$CD_2CD(Ph)$ was much lower for the triflate than for the perchlorate. This indicates that for triflates deprotonation proceeds more rapidly than initiation. The perchlorate anion is more nucleophilic than the triflic anion, and therefore perchlorate esters are stable at low temperatures. Nevertheless some deprotonation occurred, as manifested by the formation of the nondeuteriated polystyrene from the ester as well as the unsaturated oligomers.

Perchlorate esters are stable at −78 °C but participate in Friedel–Crafts alkylation at temperatures above −40 °C.

This reaction is catalyzed by the perchloric acid since in the presence of the hindered pyridine, which is an effective trap of protonic acids, the formation of the alkylation products was suppressed. On the other hand, in the presence of pyridine, unsaturated oligomers were found due to the abstraction of β-hydrogen atoms or trapping, the acid being in equilibrium with olefinic end groups.

Perchlorate esters are sensitive to the presence of water and form the corresponding ethers. Why is the kinetics of polymerization only slightly influenced by water? The first product of the reaction with water, a protonated carbinol, is reversibly protonated and releases the perchloric acid. The carbinol subsequently reacts with growing ester, forming an ether and the perchloric acid:

$$-CH_2CH(Ph)OClO_3 + H_2O \rightarrow -CH_2CH(Ph)O^+HH,\ ClO_4^- \rightleftharpoons -CH_2CH(Ph)OH + HClO_4$$

$$-CH_2CH(Ph)OH + -CH_2CH(Ph)OClO_3 \rightarrow -CH_2CH(Ph)O^+(H)CH(Ph)CH_2-,\ ClO_4^- \rightleftharpoons -CH_2CH(Ph)OCH(Ph)CH_2- + HClO_4$$

Thus, the reaction with a small amount of water resembles the transfer rather than termination reaction. On the other hand, in the polymerization coinitiated by Lewis acid, counterions have a complexed structure (MtX_nY^-), and they can abstract a proton from neither protonated carbinol nor ether. Thus, they cannot reinitiate polymerization. This can explain a big difference between polymerization initiated by protonic and Lewis acids. Protonic acids form more basic anions, which have a higher affinity toward the proton.

Although our results show the presence of covalent species during polymerization they do not prove pseudocationic polymerization. It seems that some fraction of the esters was deprotonated, and the direct incorporation of the nondeuteriated end groups could occur by the covalent mechanism or by the preliminary ionization and a monomer addition to the ionic species followed by the rapid collapse of counterions to a covalent ester.

It seems that covalent esters are activated by traces of the protonic acids. This activation is manifested not only in the alkylation reaction but also in the more rapid consumption of the ester and the monomer in the absence of the hindered pyridine. Very recently we have observed the activation of 1-phenylethyl trifluoroacetate by trifluoroacetic acid.[23] This ester alone cannot initiate polymerization of styrene.[24,25] The activation proceeds by the formation of intermediate ionic species because the rate of incorporation of the ester into polymer chains is much slower than the rate of racemization of optically active ester.[23] The complete loss of optical activity in the polymer indicates that the incorporation of the trifluoroacetate ester does not proceed by a multicenter rearrangement but by the ionic intermediates. The attempts to prepare the optically active 1-phenylethyl perchlorate and to study the mechanism of its incorporation into the polymer chain were unsuccessful.

To our best knowledge the observation of the macromolecular ester is the first NMR observation of the growing species in the polymerization of styrenes. Usually the chemical shifts of model active centers are very similar to those in the polymerization system. For example, the difference in chemical shifts in the growing onium ions in polymerization of tetrahydrofuran, oxepane, or thietanes and the corresponding model compounds is less than 0.1 ppm.[26] We have observed 0.5 ppm shielding of the macromolecular ester in comparison with 1-phenylethyl perchlorate. This does not indicate any difference in the chemical reactivity between these species but solely the magnetic shielding by the adjacent aromatic nucleus.

A similar effect was found for the 1-phenylethyl chloride and the corresponding oligomeric chlorides. The difference was 0.45 and 0.50 ppm for the meso or racemic dimer and 0.48 ppm for the trimer. Identical effects were observed in the oligomerization of styrene by trifluoroacetic acid in CCl_4 solvent.[22] In dimeric species the extended zigzag conformation leads to stronger shielding in the racemic dyad. The differences in the energy level of different conformers decrease for higher oligomers as calculated for 2,4,6-triphenylheptanes.[27] A higher number of possible conformers and shielding by more remote aromatic rings lead to broader absorption for the species with a degree of polymerization higher than 2. Thus, any future NMR search for the active species in the polymerization of styrenes should taken into account the ring currents from the adjacent aromatic nuclei.

Acknowledgment. Financial support for this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. $PhCH(CH_3)OClO_3$, 2815-29-4; $PhCH{=}CH_2$, 100-42-5; $HClO_4$, 7601-90-3; H_2O, 7732-18-5; 2,6-di-*tert*-butyl-4-methylpyridine, 38222-83-2.

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